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Subject: Hr Pesticide method summary



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**DETERMINATION OF
ORGANOCHLORINE PESTICIDES BY HRGC/HRMS**

Extraction and Cleanup Procedures

This method is applicable to the analysis of solids, tissues (including milk and blood), aqueous samples, XAD columns, air samples and solvent extracts. Samples are spiked with a suite of isotopically labelled surrogate standards prior to analysis. Samples are solvent extracted. The extracts are cleaned up and separated into two fractions, E1 and E2, using Florisil. Each fraction is spiked with isotopically labelled recovery (internal) standard(s) prior to analysis for a suite of organochlorine pesticides by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

HRGC/HRMS Analysis

Analysis of the E1 and E2 fractions is performed on a high-resolution mass spectrometer (HRMS) coupled to a high-resolution gas chromatograph (HRGC) equipped with a J&W DB-5 chromatography column (60 m, 0.25 mm i.d., 0.10 µm film thickness). The HRMS is operated at a static (8000) mass resolution (10% valley) in the electron ionization (EI) mode using multiple ion detection (MID). The ions acquired are presented in Tables 1 and 2.

Initial calibration is performed using a multi-point calibration series of solutions that encompass the working concentration range. Calibration is verified at least once every twelve hours by analysis of a mid-level calibration solution

Analyte Identification

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak response must be at least three times the background noise level.
2. The peak retention time must be within the window predicted from the initial calibration runs and the surrogate standard retention times.
3. Peak maxima for quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 20% of the theoretical except for oxychlordane and labelled methoxychlor that must be 30% and 50% respectively.

Quantification Procedures

Target concentrations are determined with respect to labelled surrogate standards as shown in Tables 1 and 2. Mean relative response factors (RRF) determined from the initial calibration runs are used to convert raw peak areas in sample chromatograms to final concentrations as follows:

$$\text{Concentration of Target} = \left(\frac{\text{area of Target}}{\text{area of Surrogate}} \right) \times \left(\frac{\text{weight of Surrogate}}{\text{RRF}} \right) \times \left(\frac{1}{\text{weight of sample}} \right)$$

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$$\text{where } \text{RRF} = \left(\frac{\text{area of Target}}{\text{area of Surrogate}} \right) \times \left(\frac{\text{concentration of Surrogate}}{\text{concentration of Target}} \right)$$

Final concentrations are recovery corrected by the method of quantification.

Sample specific detection limits (SDLs), reported with the analytical results, are determined from the analysis data by converting the minimum detectable signal to a concentration following the same procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as three times the height of the noise in the m/z channel of interest, converted to an area using the area height ratio of the corresponding labelled surrogate peak.

Recoveries of surrogates are determined similarly against the recovery (internal) standard and are used as general indicators of overall analytical quality.

QA/QC

Samples are analyzed in batches consisting of a maximum of twenty samples, a procedural blank and a spiked matrix (OPR) sample. Sample duplicates or matrix spike/matrix spike duplicate (MS/MSD) pairs may be analyzed on an individual contract basis. The batch is carried through the complete analytical process as a unit. For sample data to be reportable, the batch QC data must meet the established acceptance criteria presented on the analysis reports.

All aspects of the method are described in detail in AXYS' document MLA-028 "Organochlorine Pesticides by Isotope Dilution HRGC/HRMS".

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Table 1. Analyte Ions Monitored, Surrogates Used, and RRF Determination for E1 Pesticides by HRGC/HRMS

(No entry in the "RRF Used" field designates an RRF derived from that same compound.)

Analyte Name	Conc. in Sample (ppm)	Quantified against Labeled standard	RRF Determination	mass1	mass2	m ₁ /m ₂ Ratio	Ion Ratio Tolerance (± %)
1,3/1,4-Cl ₂ -BZ		¹³ C ₆ -1,4-Cl ₂ -BZ		145.969	147.966	1.56	20
1,2-Cl ₂ -BZ		¹³ C ₆ -1,4-Cl ₂ -BZ		145.969	147.966	1.56	20
1,3,5-Cl ₃ -BZ		¹³ C ₆ -1,2,3-Cl ₃ -BZ		179.93	181.927	1.03	20
1,2,4-Cl ₃ -BZ		¹³ C ₆ -1,2,3-Cl ₃ -BZ		179.93	181.927	1.03	20
1,2,3-Cl ₃ -BZ		¹³ C ₆ -1,2,3-Cl ₃ -BZ		179.93	181.927	1.03	20
1,2,4,5/3,5-Cl ₄ -BZ		¹³ C ₆ -1,2,3,4-Cl ₄ -BZ		213.891	215.888	0.77	20
1,2,3,4-Cl ₄ -BZ		¹³ C ₆ -1,2,3,4-Cl ₄ -BZ		213.891	215.888	0.77	20
Cl ₅ -BZ		¹³ C ₆ -Cl ₅ -BZ		247.852	249.849	0.62	20
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HCB		¹³ C ₆ -HCB		283.81	285.807	1.25	20
TCMX		¹³ C ₆ -HCB		241.922	243.919	0.78	20
Cl ₆ -Butadiene		¹³ C ₆ -1,2,3,4-Cl ₄ -BZ	1,2,3,4-Cl ₄ -BZ	189.872	187.875	1.32	20
alpha-HCH		¹³ C ₆ -gamma-HCH		216.915	218.912	0.77	20
beta-HCH		¹³ C ₆ -beta-HCH		216.915	218.912	0.77	20
gamma-HCH		¹³ C ₆ -gamma-HCH		216.915	218.912	0.77	20
delta-HCH ¹		¹³ C ₆ -delta-HCH		216.915	218.912	0.77	20
Heptachlor		¹³ C ₁₀ -Heptachlor		271.81	273.81	1.24	20
Aldrin		¹³ C ₁₂ -Aldrin		262.857	264.854	1.55	20
Octachlorostyrene		¹³ C ₁₀ -trans-Chlordane		270.844	272.841	0.62	20
Oxychlordane		¹³ C ₁₀ -Oxychlordane		262.857	264.854	1.55	20
trans-Chlordane		¹³ C ₁₀ -trans-Chlordane		271.81	273.807	1.24	20
cis-Chlordane		¹³ C ₁₀ -trans-Chlordane		271.81	273.807	1.24	20
p,p-DDE		¹³ C ₁₂ p,p-DDE		246	247.997	1.56	20
p,p-DDE		¹³ C ₁₂ p,p-DDE		246	247.997	1.56	20
trans-Nonachlor		¹³ C ₁₀ -trans-Nonachlor		271.81	273.807	1.24	20
cis-Nonachlor		¹³ C ₁₀ -cis-Nonachlor		271.81	273.807	1.24	20
p,p-DDD		¹³ C ₁₂ o,p-DDT		235.008	237.005	1.56	20
p,p-DDD		¹³ C ₁₂ o,p-DDT		235.008	237.005	1.56	20
p,p-DDT		¹³ C ₁₂ o,p-DDT		235.008	237.005	1.56	20
p,p-DDT		¹³ C ₁₂ p,p-DDT		235.008	237.005	1.56	20
Photomirex		¹³ C ₁₀ -Mirex	Mirex	269.813	271.81	0.52	20
Mirex		¹³ C ₁₀ -Mirex		269.813	271.81	0.52	20

¹ delta-HCH normally will elute primarily in the E2 fraction and can be quantified solely from this fraction. Recoveries of ¹³C-delta-HCH may be reported as the sum of the E1 and E2 recoveries if significant concentrations of ¹³C-delta-HCH are observed in the E1 fraction.

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Table 1 (Cont'd)

Analyte Name	Nominal Amount Spiked (ng)	Quantified against labelled standard	RRF Determination	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance +/-
Surrogate Standards							
¹³ C ₆ -1,4-Cl ₂ -BZ	8	¹³ C ₁₂ -PCB-52		151.989	153.986	1.56	20
¹³ C ₆ -1,2,3-Cl ₃ -BZ	8	¹³ C ₁₂ -PCB-52		185.95	187.947	1.03	20
¹³ C ₆ -1,2,3,4-Cl ₄ -BZ	8	¹³ C ₁₂ -PCB-52		221.908	223.905	2.08	20
¹³ C ₆ -Cl ₅ -BZ	8	¹³ C ₁₂ -PCB-52		255.869	257.866	1.55	20
¹³ C ₆ -HCB	8	¹³ C ₁₂ -PCB-52		289.83	291.828	1.25	20
¹³ C ₆ -beta-HCH	8	¹³ C ₁₂ -PCB-52		222.935	224.932	0.77	20
¹³ C ₆ -gamma-HCH	8	¹³ C ₁₂ -PCB-52		222.935	224.932	0.77	20
¹³ C ₆ -delta-HCH	8	¹³ C ₁₂ -PCB-52		222.935	224.932	0.77	20
¹³ C ₁₀ -Heptachlor	8	¹³ C ₁₂ -PCB-138		276.827	278.824	1.24	20
¹³ C ₁₀ -Aldrin	8	¹³ C ₁₂ -PCB-138		269.88	271.877	1.55	20
¹³ C ₁₀ -Oxychlordane	8	¹³ C ₁₂ -PCB-138		269.88	271.877	1.55	30
¹³ C ₁₀ -trans-Chlordane	8	¹³ C ₁₂ -PCB-138		276.827	278.824	1.24	20
¹³ C ₁₀ -trans-Nonachlor	8	¹³ C ₁₂ -PCB-138		276.827	278.824	1.24	20
¹³ C ₁₀ -cis-Nonachlor	8	¹³ C ₁₂ -PCB-138		276.827	278.824	1.24	20
¹³ C ₁₂ -o,p-DDE	8	¹³ C ₁₂ -PCB-138		258.041	260.038	1.56	20
¹³ C ₁₂ -p,p-DDE	8	¹³ C ₁₂ -PCB-138		258.041	260.038	1.56	20
¹³ C ₁₂ -o,p-DDT	8	¹³ C ₁₂ -PCB-138		247.048	249.045	1.56	20
¹³ C ₁₂ -p,p-DDT	8	¹³ C ₁₂ -PCB-138		247.048	249.045	1.56	20
¹³ C ₁₀ -Mirex	8	¹³ C ₁₂ -PCB-138		276.827	278.824	1.25	20
Recovery Standards							
¹³ C ₁₂ -PCB-52	10			301.963	303.96	0.77	20
¹³ C ₁₂ -PCB-138	10			299.947	301.944	0.77	20

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Table 2. Analyte Ions Monitored, Surrogates Used and RRF Determination for E2 Pesticides by HRGC/HRMS

(No entry in the "RRF Used" field designates an RRF derived from that same compound.)

Analyte Name	Nominal Amt Spiked (µg/ml)	Quantified against Labelled Standard	RRF Determination	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance (%)
delta-HCH		¹³ C ₆ -gamma-HCH		216.915	220.909	1.63	20
Heptachlor epoxide		¹³ C ₉ -Heptachlor-Epoxide		354.841	352.844	0.8	20
alpha-Endosulphan		¹³ C ₉ -alpha-endosulphan		264.854	262.857	0.64	20
Dieldrin		¹³ C ₁₂ -Dieldrin		264.854	262.857	0.64	20
Endrin		¹³ C ₁₂ -Endrin		264.854	262.857	0.64	20
beta-Endosulphan		¹³ C ₉ -beta-Endosulphan		264.854	262.857	0.64	20
Endosulphan sulphate		¹³ C ₉ -beta-Endosulphan		264.854	262.857	0.64	20
Endrin aldehyde		¹³ C ₁₂ -Endrin		346.896	344.899	0.64	20
Endrin ketone		¹³ C ₁₂ -Endrin		318.901	316.904	0.64	20
Methoxychlor		¹³ C ₁₂ -Methoxychlor		228.111	227.107	0.17	20
Labelled Surrogates							
¹³ C ₆ -gamma-HCH	8	¹³ C ₁₂ -PCB-153		222.935	224.932	0.78	20
¹³ C ₉ -Heptachlor-Epoxide	8	¹³ C ₁₂ -PCB-153		364.875	362.878	0.8	20
¹³ C ₉ -alpha-endosulphan	8	¹³ C ₁₂ -PCB-153		271.877	269.88	0.64	20
¹³ C ₁₂ -Dieldrin	8	¹³ C ₁₂ -PCB-153		271.877	269.88	0.64	20
¹³ C ₁₂ -Endrin	8	¹³ C ₁₂ -PCB-153		271.877	269.88	0.64	20
¹³ C ₉ -beta-Endosulphan	8	¹³ C ₁₂ -PCB-153		271.877	269.88	0.64	20
¹³ C ₁₂ -Methoxychlor	8	¹³ C ₁₂ -PCB-153		239.148	240.151	30	50
Recovery Standard							
¹³ C ₁₂ -PCB-153	10			299.947	301.944	0.78	20